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Potentiometric EDTA titrations using a bismuth amalgam electrode as indicator

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POTENTIOMETRIC EDTA TITRATIONS USING A BISMUTH AMALGAM ELECTRODE AS INDICATOR

by

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ABSTRACT

Previous work in the field of potentiometric titrations using bismuth-mercury electrodes with ethylenediaminetetraacetic acid as the titrant have been largely reproduced.

The bismuth amalgam electrode has been further developed to provide ease of preparation and maintenance and through improved techniques of cleaning to eliminate electrode poisoning effects. Various titrations have been studied to determine the solution conditions necessary for maximum end point breaks, good electrode poise, and rapid and steady equilibrium of the electrode. These conditions have been adapted to make the electrode suitable for use with automatic titration equipment and for the analysis of multicomponent mixtures.

INTRODUCTION

A reaction may serve as the basis of a titration procedure if the following conditions are met:

1. The reaction must proceed stoichiometrically.

2. Its thermodynamics must be favorable so that the reaction goes essentially to completion.

3. It must have fast kinetics.

Ordinary complex formation often fails to satisfy these conditions, especially the first. Ligands such as NH_3 and CN^- replace the water molecules in the hydration sheath in a series of discrete steps resulting in the formation of a sequence of different complex species of the type MA, MA_2,...MA_n where M is the metal ion and A is the ligand. It is possible that all members of such a series will be present simultaneously greatly complicating the stoichiometry.

The use of ethylenediaminetetraacetic acid (EDTA) as the titrant provides a much more straightforward state of affairs since all the ligands needed by any one metal atom are linked together in one molecule. Such a hexadentate ligand eliminates the step-wise complex formation characteristic of many other compounds and thereby simplifies the stoichiometry of the process.

The end point of such a titration can be detected by a variety of means which are sensitive to either the EDTA or the metal ion present. This work deals with end point detection by means of observing the change in potential at an electrode sensitive to the changing concentration of metal ion in solution. Specifically, this research is the culmination of work done by Reilley(1), who developed the first effective electrode that was responsive to the metal ion concentration in EDTA titrations: the mercury pool electrode.

Improvements on the mercury pool electrode by Legg (2) evolved a mercury-bismuth slurry electrode which yielded much greater potential breaks at the end point and a bismuth amalgam electrode. Further progress initiated by Isbell (3) made the bismuth amalgam electrode hold out the prospect of being the simplest and most effective electrode of all.

The present work extends the development of the bismuth amalgam electrode to the point where predictable and reproducible results can be obtained without undue dependence upon unique characteristics of an individual electrode. The electrode is therefore suitable for use on automatic titration equipment and for the analysis of some multicomponent mixtures.

HISTORICAL BACKGROUND

Much of the early work in the field of complexometric titrations was performed by Schwarzenbach (4) at the Eidgenössische Technische Hochschule in Zurich in the late Fourties and early Fifties. It was during this period that he discovered the remarkable stability of complexes formed between certain organic compounds and metal ions and immediately foresaw their applicability as powerful tools in the area of chemical analysis.

Since it is capable of forming the most stable complexes with the widest range of metals, ethylenediaminetetraacetic acid (EDTA)* has become the most successful of these compounds. It has the following structure:

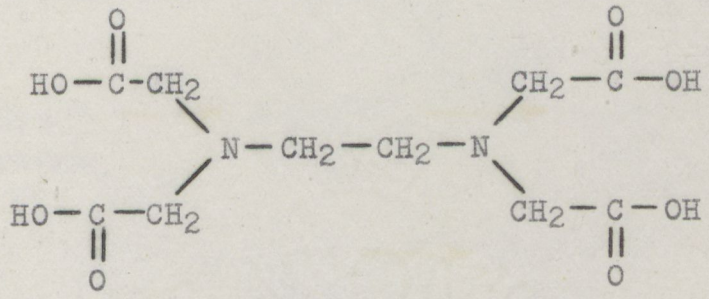

Figure 1
Structure of EDTA

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*EDTA is also known as ethylenedinitrilotetraacetic acid. The di-sodium salt is quite stable and available in high purity. Dried at 80° it can be a primary standard.

With metal ions, EDTA is capable of forming four salt-like bonds through the acidic oxygen atoms and two coordinate bonds through the nitrogen atoms and is accordingly designated as a hexadental chelating agent. The term chelate is, incidentally, derived from the Greek "chelos" meaning claw. The name is thus a particularly vivid interpretation of the manner in which EDTA clutches hapless metal ions.

Schwarzenbach achieved the first practical means of end point detection for EDTA titrations when he discovered that certain highly colored complexing agents could be used as metal indicators. These organic compounds, most of which vary their chromophoric properties as the molecular or ionic forms alter their degree of protonation with variations in pH, are one color in the unmetallized form and a different color when complexed. These changes are shown in equation (1).

$$\underset{\text{orange}}{Dye^{-m}} \xrightarrow{nH^+} \underset{\text{blue}}{H_nDye^{n-m}} \xrightarrow{m-nH^+} \underset{\text{red}}{H_mDye} \qquad (1a)$$

$$M^{+n} + \underset{\text{green}}{Dye^{-m}} \longrightarrow \underset{\text{pink}}{M \cdot Dye^{n-m}} \qquad (1b)$$

A small amount of such an indicator when added to a solution of metal ion to be titrated will remain complexed with the metal until the end point where it may be

displaced by the titrant if that chelon forms a more stable complex than the indicator.

However, in reaction (1b) the metal-dye complex must be of just the right stability. If the dye complex is too stable, late or no end points are obtained. If the metal-dye complex is too weak, early end points are obtained. Unfortunately these effects can only occasionally be remedied by changing the chelon titrant used. In addition, a given metal indicator dye is generally useful for only a few metal ions, and then under limited conditions of pH and buffer type. One final limitation occurs when the metal ion or complex is highly colored such as chromium, vanadyl, or copper.

To remedy such limitations, a variety of instrumental end point detection techniques were formulated. A polarographic determination of EDTA was first accomplished by Turners and others (5) in 1949. The field was relatively quiescent until a flurry of discoveries in 1954 when Laitenen and Sympson (6) reported the use of amperometric titrations, Blaedel (7) used high frequency titration methods, and Hall with his co-workers employed conductometric techniques. This same year saw the development of photometric titrations as expressed in Flaschka (9). Perhaps the most significant analytical technique to come out of this period was the use of potentiometric

apparatus to follow EDTA titrations which occurred in 1955.

Siggia and others (10), enlarging upon previous work of very limited success in potentiometry using platinum electrodes, managed to achieve reasonably good results by plating the platinum with mercury. Not long after, Reilley and his associates at the University of North Carolina (1) (11), who had already contributed to the field of coulometric EDTA titrations (12), devised the mercury pool indicator electrode which has proven to be the most useful in complexometric titrations since with it one is able to analyze most of the common metals and also the rare earths.

Improvements on Reilley's electrode were first attempted by Legg (2). His system consisted of a five per cent slurry of bismuth in mercury in Reilley's J-tube electrode. Despite encouraging results, two debilitating shortcomings were noted: the electrode displayed definite poisoning effects after repeated titrations, becoming insensitive to changes in solution; and it was extremely sluggish in reaching an equilibrium potential especially at the end point.

Further work by Isbell (3) predicated a workable bismuth amalgam electrode which did not exhibit such pronounced poisoning effects but which was still very slow in reaching a steady equilibrium potential. His electrode

also showed erratic behavior due to irregular surface conditions.

THEORY

Bismuth, in contact with a metal ion solution, M^{+n}, and a small amount of bismuth III - EDTA complex, BiY^{-1}, has the half cell potential of the cell:

$$Bi^{o} \mid BiY^{-1}, MY^{n-4}, M^{+n} \qquad (2)$$

where Y^{-4} is the completely dissociated EDTA. The potential for such a system can be found by combining the Nernst equation for Bi^{+3} at a metallic bismuth electrode

$$E = E^{o}_{Bi} + 0.0197 \log \left[Bi^{+3}\right] \qquad (3)$$

with equations for the stability constants of the reactions:

$$Bi^{+3} + Y^{-4} \rightleftharpoons BiY^{-1} \qquad (4)$$

$$M^{+n} + Y^{-4} \rightleftharpoons MY^{n-4} \qquad (5)$$

which are:

$$K_{BiY} = \frac{\left[BiY^{-1}\right]}{\left[Bi^{+3}\right]\left[Y^{-4}\right]} \qquad (6)$$

$$K_{MY} = \frac{\left[MY^{n-4}\right]}{\left[M^{+n}\right]\left[Y^{-4}\right]} \qquad (7)$$

Solving equations (6) and (7) for $[Bi^{+3}]$ and $[Y^{-4}]$ and substituting above into the Nernst equation (3) gives at 25° C:

$$E = E^{\circ}_{Bi} + 0.0197 \log \frac{[M^{+n}][BiY^{-1}]\, K_{MY}}{[MY^{n-4}]\, K_{BiY}} \qquad (8)$$

The ratio K_{MY} / K_{BiY} will obviously remain constant for a given metal. In addition, the bismuth-EDTA concentration can be considered constant near the small range at the end point since only a small amount is added prior to titration and the complex is very stable.

It can be seen, therefore, that the potential will depend only upon the ratio $[M^{+n}] / [MY^{n-4}]$. In the same manner as in a normal potentiometric titration where the end point break is caused by a large change in the ratio $[Ox] / [Red]$, this ratio will show the greatest change in the immediate vicinity og the equivalence point where the metal ion concentration will pass through several powers of ten.

The preceding derivation has shown that a bismuth electrode can be sensitive to the concentration of metal ion in a complexometric titration, but this is under ideal circumstances without taking into consideration side reactions or actual solution conditions. For this reason

the reaction between the metal ion and EDTA is studied in some detail below. The stability constant or equilibrium constant for this reaction was given by equation (7) as:

$$K_{MY} = \frac{[MY^{n-4}]}{[M^{+n}][Y^{-4}]} \qquad (7)$$

This equilibrium constant is expressed only in terms of the EDTA that is present in the completely dissociated form Y^{-4}. However, at pH values below 10, EDTA will be present in the protonated forms HY^{-3}, H_2Y^{-2}, H_3Y^{-1}, and H_4Y. These species vary in their amounts according to the acidity of the solution.

To account for this fact, the stability constant under the actual solution conditions must be calculated to give the apparent stability constant. At any pH, this can be expressed as:

$$K_{app} = \frac{[MY^{n-4}]}{[M^{+n}][Y]^*} = \frac{[MY^{n-4}]}{[M^{+n}][Y^{-4}]\ a_H} \qquad (9)$$

where $[Y]^*$ denotes the total concentration of EDTA not combined with the metal but including all its forms. This $[Y]^*$ may be related to $[Y^{-4}]$ by the expressions:

$$[Y]^* = [Y^{-4}] + [HY^{-3}] + [H_2Y^{-2}] + [H_3Y^{-1}] + [H_4Y] \quad (10a)$$

or $$[Y]^* = [Y^{-4}]a_H \quad (10b)$$

Each of the factors in (10b) can be formulated in terms of their respective stability constants as follows:

$$K_1 = \frac{[HY^{-3}]}{[Y^{-4}][H^+]} \quad \text{or} \quad [HY^{-3}] = K_1[Y^{-4}][H^+] \quad (11)$$

$$K_2 = \frac{[H_2Y^{-2}]}{[HY^{-3}][H^+]} \quad \text{or} \quad [H_2Y^{-2}] = K_2[HY^{-3}][H^+] \quad (12)$$

$$K_3 = \frac{[H_3Y^{-1}]}{[H_2Y^{-2}][H^+]} \quad \text{or} \quad [H_3Y^{-1}] = K_3[H_2Y^{-2}][H^+] \quad (13)$$

$$K_4 = \frac{[H_4Y]}{[H_3Y^{-1}][H^+]} \quad \text{or} \quad [H_4Y] = K_4[H_3Y^{-1}][H^+] \quad (14)$$

Substituting the results of equations (11-14) into (10) and then resubstituting further in the same manner for all protonated forms of EDTA other than $[Y^{-4}]$ gives

$$[Y]^* = [Y^{-4}] + K_1[Y^{-4}][H^+] + K_{1,2}[Y^{-4}][H^+]^2 + K_{1,2,3}[Y^{-4}][H^+]^3 + K_{1,2,3,4}[Y^{-4}][H^+]^4 \quad (15)$$

The factor a_H can be determined from equation (10b) by substituting the terms on the right of equation (15) for

$[Y]^*$ and dividing by $[Y^{-4}]$ so that

$$a_H = 1 + K_1[H^+] + K_{12}[H^+]^2 + K_{123}[H^+]^3 + K_{1234}[H^+]^4 \quad (16)$$

The stability constants of the various forms of EDTA have been measured by Schwarzenbach (4) so that the values of a_H can be calculated at any pH. It varies in a direct exponential fashion with the hydrogen ion concentration. The important point to note is that a_H is approximately equal to unity at pH values above 10.

Another complication that must be considered in the reaction of metal ion and EDTA is the presence of additional complex forming substances besides EDTA. This additional complexone is present because most metal ions precipitate in alkaline solution unless they are complexed to some extent with a buffer or purposefully added chelon. The precipitate itself would not be injurious from the thermodynamic standpoint, but the kinetics of the reaction between chelons and precipitates are slow. Better results are obtained therefore if the precipitate is eliminated through use of the complex effect.

In such an instance, $[M^{+n}]$ in the stability constant equation (7) can no longer be considered the total amount of "free" metal ion, although it is the total amount not complexed with EDTA if a factor b_A is included. The effect of an auxiliary complexing agent A can be determined

following the same mathematical procedure as for the pH effect except that stability constants of the various complexes between M and A are used such as

$$K_n = \frac{[MA_n]}{[MA_{n-1}][A]} \qquad (17)$$

instead of the similiar constants for the various forms of EDTA. The apparent stability constant taking the complex effect into account is:

$$K_{app} = \frac{[MY^{n-4}]}{[M]^*[Y^{-4}]} \text{ or } K_{app} = \frac{[MY^{n-4}]}{b_A[M^{+n}][Y^{-4}]} \qquad (18)$$

The factor b_A has been shown by Flaschka (9) to vary in direct exponential proportion to the concentration of the auxiliary complexing agent. Its value becomes unity when there is no auxiliary chelon present thus providing the maximum value of the apparent stability constant.

A consideration of the effects of pH and additional complex forming substances simultaneously gives the final combined form of the apparent stability constant as:

$$K_{app} = \frac{[MY^{n-4}]}{[M^{+n}][Y^{-4}]a_H b_A} \text{ or } K_{app} = \frac{K}{a_H b_A} \qquad (19)$$

This indicates that for the maximum stability and therefore the greatest end point breaks in an EDTA titration,

an optimum balance must be found which maximizes the pH while using the minimum amount of auxiliary complexing agent to keep the metal ion in solution.

Since the apparent stability constant changes with variations in the pH of the solution, a buffer must be added to keep pH fluctuations to a minimum. The need for a buffer is made obvious from the following reaction:

$$M^{+n} + H_2Na_2Y \longrightarrow MY^{n-4} + 2Na^{+} + 2H^{+} \qquad (20)$$

As the metal ion is titrated, hydrogen ions are liberated from the di-sodium salt of EDTA which is the usual form of EDTA employed in titrations. The liberated hydrogen ions lower the apparent stability constant along with the pH, thereby altering the titration curve itself if no buffer is present. In most cases the buffer and auxiliary complexing agent can be combined in the same substance such as the buffer system NH_3, NH_4^{+}, thus limiting the possibility of cumulative adverse effects. Nevertheless, excess buffer must be avoided even when it has no complexing effect on the metal ion since the stability constant is influenced by changing the ionic strength. An increase in the strength of neutral salts, i.e., increase of ionic strength, decreases the stability in most cases (9).

Temperature is also expected to influence the stability constants. Higher temperatures cause complexes to break apart easier indicating that the stability is inversely proportional to temperature. The presence of organic solvents has also been shown to affect the stability constants in direct proportion to their concentration (10). Both of these effects, however, seldom have a very pronounced influence and may be ignored except in cases where extreme conditions prevail (9).

Although previous work by Reilley and his co-workers utilized a mercury electrode, bismuth was the choice of electrode material in this study. This choice can best be explained by a consideration of the Nernst equation (8) which shows that the extent of the end point break will be dependent not only upon the stability constant of the metal being titrated but also the stability constant of the electrode metal-EDTA complex. Therefore, the higher the electrode-EDTA stability constant, the better the titration results. For bismuth-EDTA the log K_{BiY} is about 26, while for the corresponding mercury complex log $K_{HgY} = 21.2$.

Although bismuth is not highly reactive with the various titration solutions, it has one serious handicap which must be overcome before it can be used as an electrode;

its relatively low positive potential which results in oxygen interference in the form of bismuth oxide. Oxygen interference can be characterized by the half-wave potential which depends somewhat on the pH and buffer type and strength. In the pH region from 3-10, its value varies between 30 and 100 millivolts versus the saturated calomel electrode. Oxygen will not interfere with titrations where the potentials are more positive than the oxygen potentials. Unfortunately, tha standard potential of bismuth is only 0.036 volts vs SCE. This situation can be rectified by amalgamating the bismuth with triply distilled mercury which inhibits oxygen interference with bismuth. The mercury itself has a positive enough potential (0.612 volts vs SCE) to eliminate oxygen interference.

Legg (2) has shown that such an amalgam electrode acquires the characteristics of the amalgamated metal while retaining much of the stability of the mercury electrode. In addition, both metals have a large hydrogen overvoltage which minimizes the possibility of evolving hydrogen from solution. For mercury this value is 0.570 volts and for bismuth it is 0.388 volts.

The only disadvantage of the bismuth amalgam electrode is its susceptibility to halide interference. Because of the formation of insoluble bismuth oxychloride and mercurous chloride, the positive potential limit may

be decreased, especially in acidic solution. Care must be taken therefore, to exclude halide ions even to the point of using an ammonium nitrate salt bridge when the calomel electrode is used as reference.

The extent of end point breaks was found by Reilley (1) not to depend on the amount of HgEDTA present in the solution to be titrated, but that only the absolute potentials shift up or down with changes in concentration. One drop of a 10^{-3}M solution is sufficient to establish a reasonably constant value for the mercury content so that trace additions of mercury ion do not seriously alter the shape of the titration curve. A higher concentration of mercury-chelonate furnishes a better poised electrode which is desirable in cases where small amounts of halide or oxygen tend to interfere; also, the shape of the titration curves becomes more symmetrical. In the same manner, addition of both BiEDTA and HgEDTA should result in a well poised electrode.

GENERAL PROCEDURE

Initially, Legg's work (2) with the bismuth-mercury slurry electrode was studied in order to gain a familiarity with chelometric titrations. A J-tube electrode was made and fitted with a 5% mixture of powdered bismuth in mercury. Several titrations using Zn^{++} solutions were run until a sufficient knowledge of the techniques involved was gained. The bismuth amalgam electrode put forth by Isbell (3), which consists of a lump of bismuth wetted with mercury suspended in a titration solution by means of an alligator clip, was then investigated by performing titrations with it.

The bismuth amalgam electrode was seen to offer the best prospect for further development, and the work has therefore progressed in this direction. The electrode has been redesigned in order to eliminate variations due to changing surface conditions and irregularities. A number of methods of cleaning the electrode have been employed to determine the simplest and most effective technique for eliminating the poisoning effects of bismuth oxide and other impurities.

The dependence of the end point break on the concentration of the metal to be titrated has been studied to determine optimum solution conditions. At

the same time, the effect of buffer concentration has been observed along with the effect of BiEDTA and HgEDTA. For all of these studies, Zn^{++} was the metal titrated. The procedure for the preparation of all solutions and electrodes is outlined in the next section.

In addition to manual titration methods, the bismuth amalgam electrode has been employed on automatic titration apparatus and the conditions necessary for the best results have been determined.

Finally, the electrode has been used to titrate Ca^{++} and Cu^{++} to prove its versatility and attempts have been made to titrate two metals in solution together.

APPARATUS USED

The saturated calomel electrode with an ammonium nitrate salt bridge shown in figure 2 was the reference electrode.

Figure 3 illustrates the "J" type mercury pool electrode prepared by Reilley (12) which was used with bismuth mercury slurries.

The bismuth amalgam electrode used almost exclusively in this work is depicted in figure 4.

The potentiometric bridge was a Leeds and Northrup Student Potentiometer serial number 1675542. Potential changes were detected by using a Leeds and Northrup galvanometer cat. no. 2435C in conjunction with the potentiometer. The galvanometer had its sensitivity decreased by the use of a 500 ohm shunt. It was further protected by the use of two telegraph key circuit connectors, one of which could divert the electrode current through a 250 ohm resistor.

A standard Kimax 50 ml burette was used during all manual titrations.

A plastic encased magnet was employd with a magnetic stirrer to maintain homogeneity in the solutions.

Automatic titrations were accomplished with a Sargent-Malmstadt spectro-electro titrator model SE serial number 017-024 and a Sargent-Malmstadt automatic titration

controller serial no. 1860.

A Photovolt model 110 electronic pH meter was used while adjusting solution acidity.

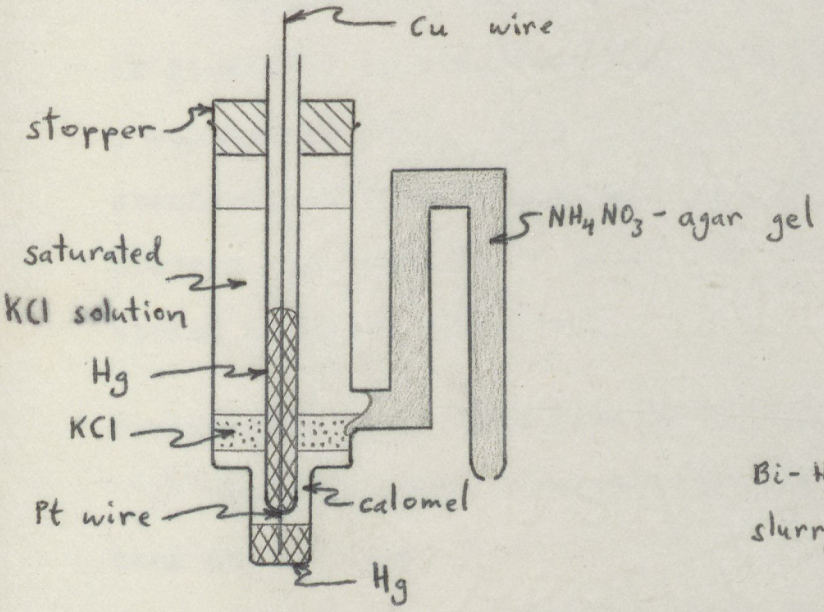


Figure 2

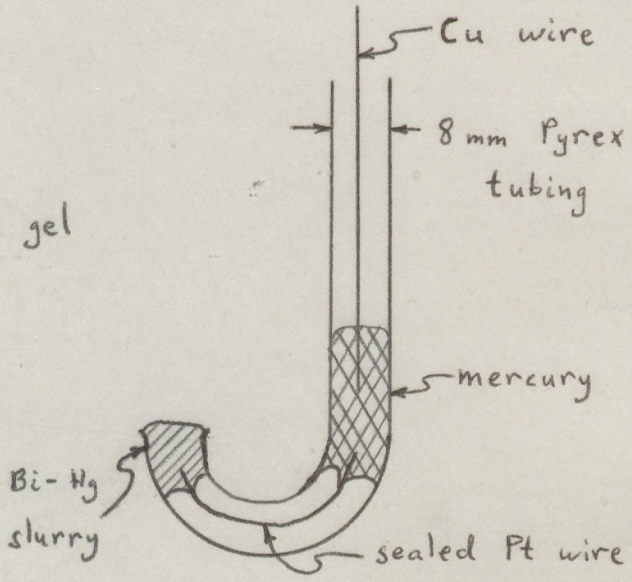


Figure 3

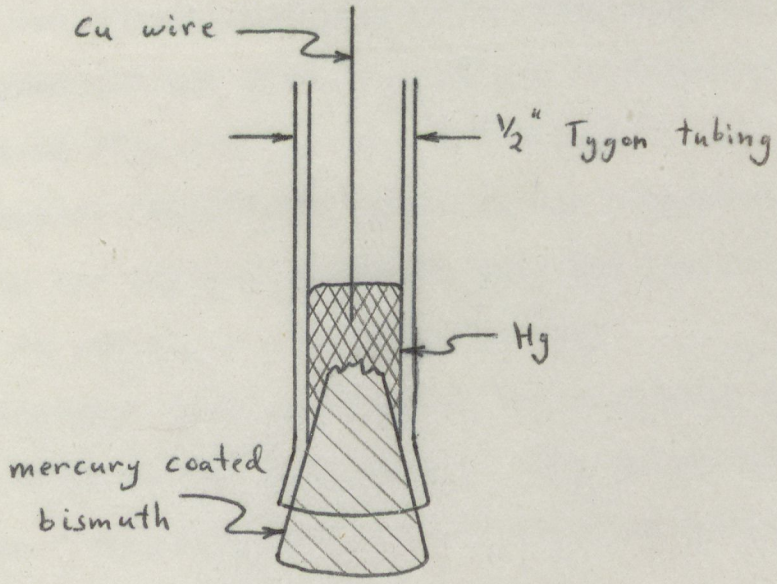


Figure 4

CHEMICALS AND REAGENTS

Preparation of 0.1 M EDTA using the di-sodium salt:

37.225 g of the salt dried at 80°C for two days is dissolved in water and then diluted to 1.0 liter in a volumetric flask. The solution, usable as a primary standard, is then transferred to a plastic bottle to prevent the leaching of metal ions that occurs when stored in glass containers.

Preparation of 0.1 M solutions of metal ions:

Reagent grade chemicals and distilled water are used exclusively.

Zinc: zinc pellets are first washed with dilute HCl and rinsed with water. They are then washed with alcohol and ether and dried. From this sample, 6.538 g are weighed out and dissolved in the minimum amount of nitric acid then diluted to 1.0 liter.

Copper: 3.177 g of electrolytic copper are dissolved in the minimum amount of HNO_3 and the solution diluted to 500 ml in a volumetric flask.

Calcium: 5.005 g of $CaCO_3$ are dissolved in the minimum amount of HNO_3 necessary. The carbon dioxide formed is then boiled off and the solution diluted to 500 ml.

Preparation of pH 10 buffer:

125 g of NH_4NO_3 is dissolved in 570 ml of concentrated ammonia and diluted with water to 1.0 liter. The resulting solution is stored in a plastic bottle for the same reasons as the EDTA solution.

Preparation of Bi-EDTA and Hg-EDTA complexes:

1.21 g of $Bi(NO_3)_3 \cdot 5H_2O$ is dissolved in nitric acid and diluted to 50 ml. To this solution is added 50 ml of 0.1 M EDTA and the mixture evaporated until crystallization begins. The crystals are separated by filtration, washed briefly with water, and enough water added to make a saturated solution which is stored in a dropping bottle.

1.36 g of $HgCl_2$ are dissolved in water and diluted to 50 ml, and then mixed with 50 ml of 0.1 M EDTA. Chloride ion is eliminated by recrystallizing the HgEDTA several times until an aliquot of the solution gives a negative chloride test with silver nitrate. The saturated solution of HgEDTA is also stored in a dropping bottle.

Preparation of bismuth-mercury slurry:

The procedure for preparing metal amalgams described in Experimental Physical Chemistry (13) was followed. In this procedure, powdered bismuth is added to triply distilled mercury under a layer of dilute sulfuric acid to form a 5% slurry.

Preparation of bismuth amalgam electrodes:

A lump of bismuth is ground into the shape of a truncated cone and polished on the buffing wheel of a grinder. The lump is then wedged snugly into either 3/8" or 1/2" Tygon tubing depending on the size of the lump which is next immersed for one hour in triply distilled mercury. The electrode can be cleaned effectively between titrations by washing with either hot 9M sulfuric acid or hot concentrated phosphoric acid. Even better results are obtained, however, if the electrode is polished for several hours with paper towels until a mirror finish is obtained. Occasional dipping of the electrode in warm 9M sulfuric acid and then rinsing with water facilitates the polishing by dissolving oxides of bismuth.

EXPERIMENTAL RESULTS

Bismuth mercury slurry as indicator electrode:

The results of a titration using Legg's bismuth mercury slurry electrode are shown in table 1 and figure 5. The potential break, while reasonably large, is not too distinct and leaves the exact location of the end point in doubt. Short of replacing the slurry with each titration, no effective means of removing contaminating impurities from the slurry has been found. This electrode is also difficult to handle due to the possibility of spillage, and finally it is not very easy to make.

Bismuth amalgam electrode as indicator:

Representative titrations involving this electrode are recorded in tables 2-9 and figures 6-11. Tables 2-6 and the accompanying figures chronolog the progress of the search for the optimum conditions of electrode preparation, buffer concentration, and metal ion concentration. Tables 7 and 8 are the titration results for copper and calcium to prove the applicability of the electrode for metals other than zinc. Under the optimum conditions, the bismuth amalgam electrode yields potential breaks of over 200 millivolts for zinc and copper and

over 170 mv for calcium. The most effective method of electrode preparation was determined to be mild washing with hot 9M H_2SO_4 and polishing with a paper towel after rinsing the acid off.

As is recommended by Reilley (12), the end point is not taken as the geometric center of the curves since they are asymmetrical, but half way up that portion of the curve which has the steepest slope. The end points found by interpolating on the curves are then used to calculate the millimoles of metal found so that a comparison may be made with the amount taken.

The speed at which the electorde came to a steady equilibrium with the solution is also shown on the tables. Even under the best conditions the electrode required four minutes to stabilize after the addition of a portion of EDTA at the end point. Nevertheless, it has been found that the electrode can pass through a 100 mv change in 75 seconds. The electrode drift in basic media was measured over a two hour period and has been found to be less than 0.1 mv per minute which is of little significance in the analysis of the titration curves.

Effect of BiEDTA and HgEDTA

Either of these two metal complexes has a large effect on the poise and speed of stabilization of the electrode when a drop of their saturated solution is

added to the titration mixture. A second drop of the metal complex added originally has virtually no effect in helping the electrode attain the minimum starting potential, while one drop of the other metal complex exerts about one third the influence of the original drop.

Effect of pH 10 buffer concentration:

The best results are obtained when 0.5-2.0 ml of buffer is added. Excessive buffer decreases the end point break and distorts the titration curve as was discussed earlier in the section on the theory of potentiometric titrations.

Effect of metal ion concentration:

Although the minimum concentration of metal ion has not been determined, the more dilute solutions (less than 0.001M) are clearly preferable. Halving the concentration of metal ion will permit the concentration of the uncomplexed metal to be several powers of ten smaller. Eventually, however, a limit is reached where the end point break can no longer be extended due to the insensitivity of the electrode to extremely low concentrations of metal ion.

Analysis of two-metal mixtures:

It was hoped that zinc or copper could be determined

in the presence of calcium by use of the pH effect which would prohibit the weak calcium-EDTA complex from forming in acid solution. However, acetate ion in the pH 5 buffer causes insoluble bismuth acetate to form, poisoning the electrode. Titration of the mixtures in table 9 does not result in separate breaks due to differences in complex stability but only a final break corresponding to the sum of these ions. Apparently all metal ions which are stable enough to form at a given pH are "levelled" to the weakest species.

Titrations on the automatic titrator:

The results from eight samples are recorded in table 10. Although one sample was accurate to within 0.3% of the actual amount of zinc present, precision has been poor due primarily to variations in the delivery rate of EDTA.

TABLE 1

Titration of Zinc Using the Bi-Hg Slurry Electrode

10 ml 0.0997M Zn^{++}, 5 ml pH 10 buffer, 50 ml water,
1 drop BiEDTA, 1 drop HgEDTA, titrate with 0.1019M EDTA

volume EDTA	E_{cell}
0.00 ml	0.208 volts
1.00	0.214
3.00	0.219
5.00	0.225
7.00	0.230
9.00	0.237
9.50	0.241
9.70	0.288
10.00	0.323
10.50	0.359
11.00	0.366

millimoles zinc taken: 0.997

found: 0.989

error: -0.9%

FIGURE 5

TITRATION OF ZINC USING THE

Bi-Hg SLURRY ELECTRODE

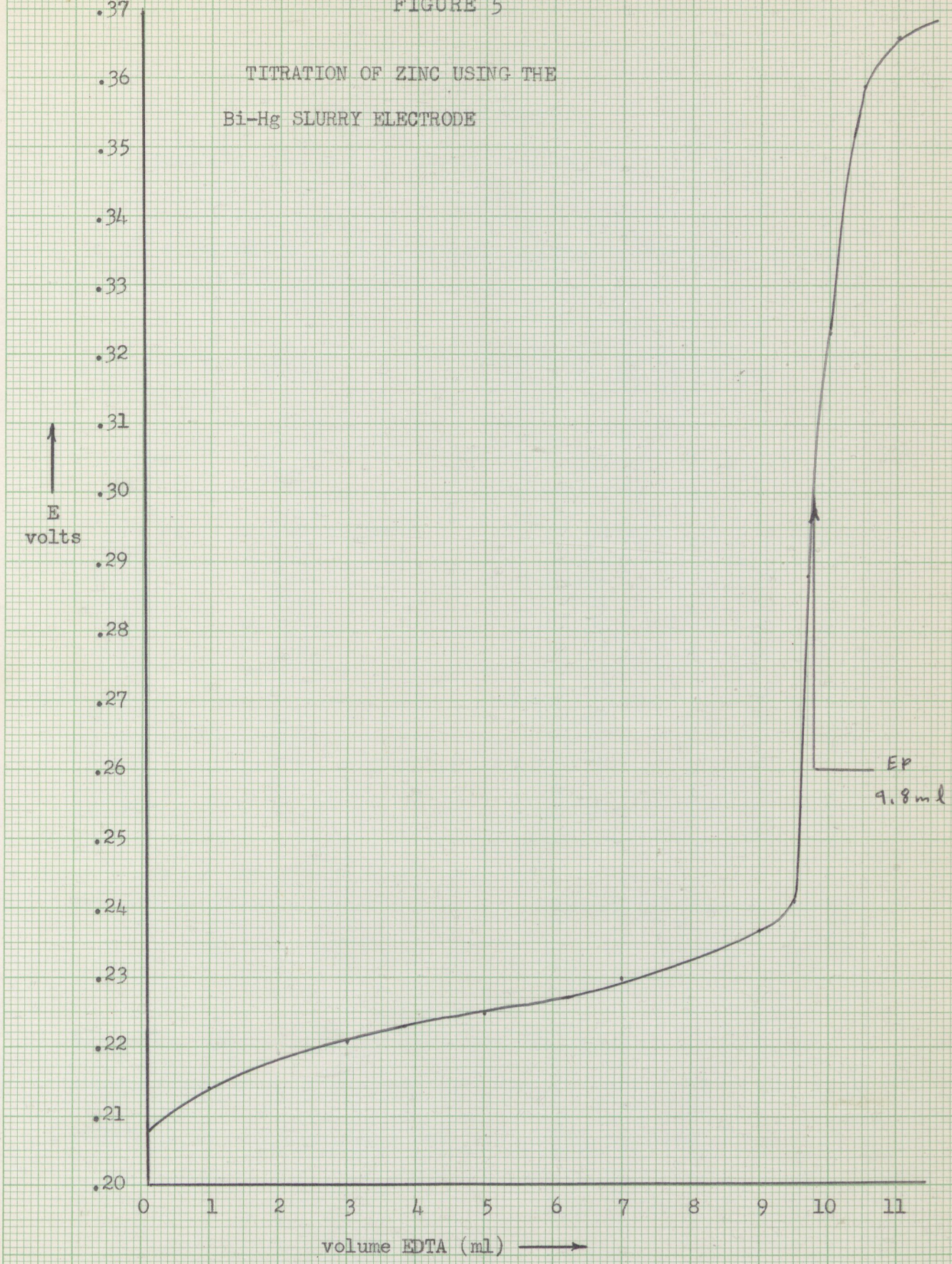


TABLE 2

Titration of Zinc

(Bismuth amalgam electrode washed with 6N HNO_3)

10 ml 0.0997M Zn^{++}, 1 drop sat BiEDTA, 1 drop sat HgEDTA, titrate with 0.1019M EDTA

10 ml pH 10 buffer
50 ml water

volume	E_{cell}
0.00 ml	0.191 volts
1.00	0.191
2.00	0.190
3.00	0.188
4.00	0.188
5.00	0.185
6.00	0.184
7.00	0.172
8.00	0.175
9.00	0.179
9.60	0.282
9.80	0.320
10.00	0.335

mmoles Zn taken: 0.997
found: 0.971
error: -2.6%

5 ml pH 10 buffer
50 ml water

volume	E_{cell}
0.00 ml	0.175 volts
2.00	0.178
3.00	0.178
4.00	0.180
5.00	0.180
6.00	0.176
7.00	0.177
8.00	0.180
9.00	0.181
9.50	0.183
9.70	0.198
9.90	0.275
10.00	0.325
10.20	0.325

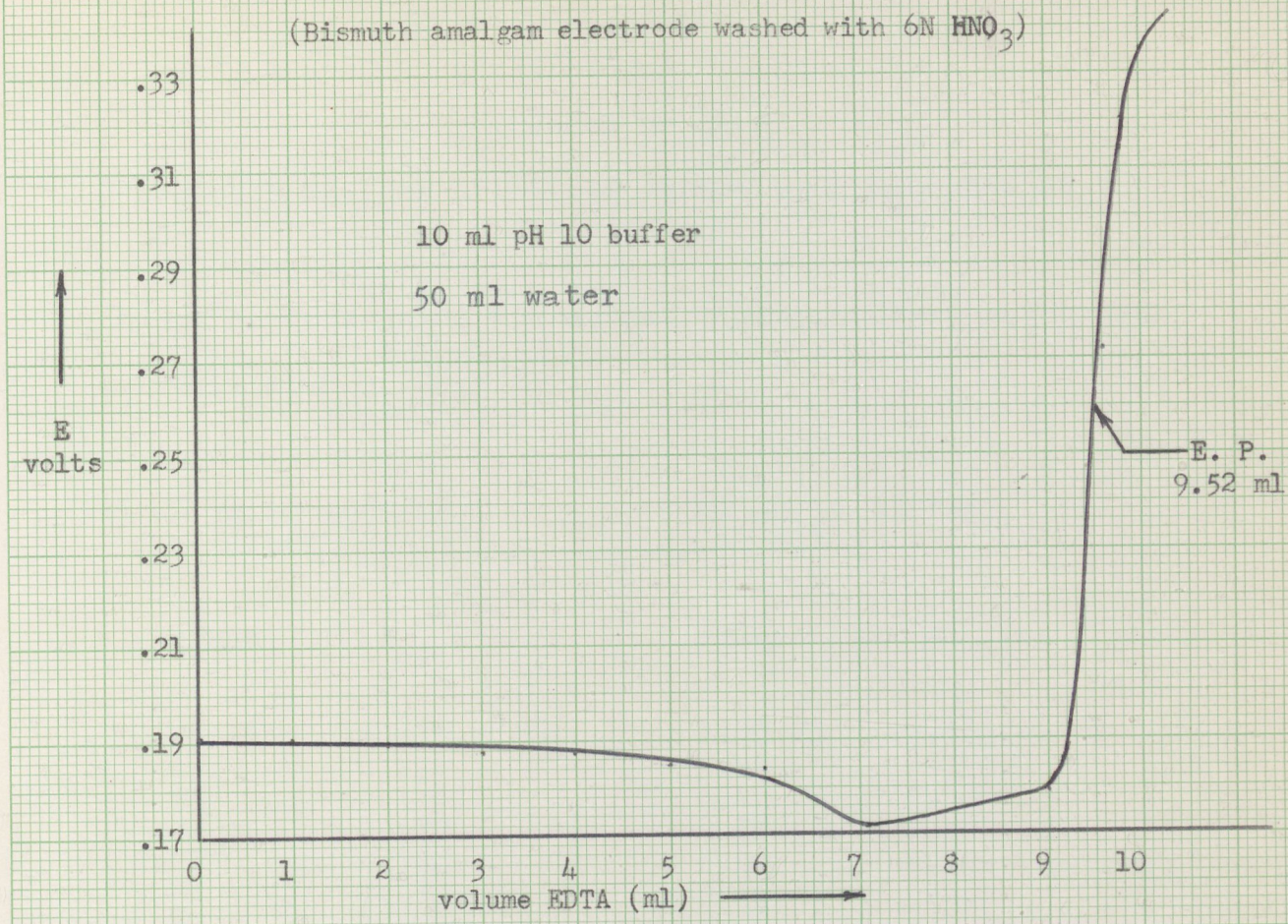
mmoles Zn taken: 0.997
found: 1.004
error: +0.7%

Remarks: The electrode required 20 minutes to come to initial equilibrium and an additional 10 minutes with each addition of titrant near the end point in both cases.

FIGURE 6

Titration of Zinc

(Bismuth amalgam electrode washed with 6N HNO_3)



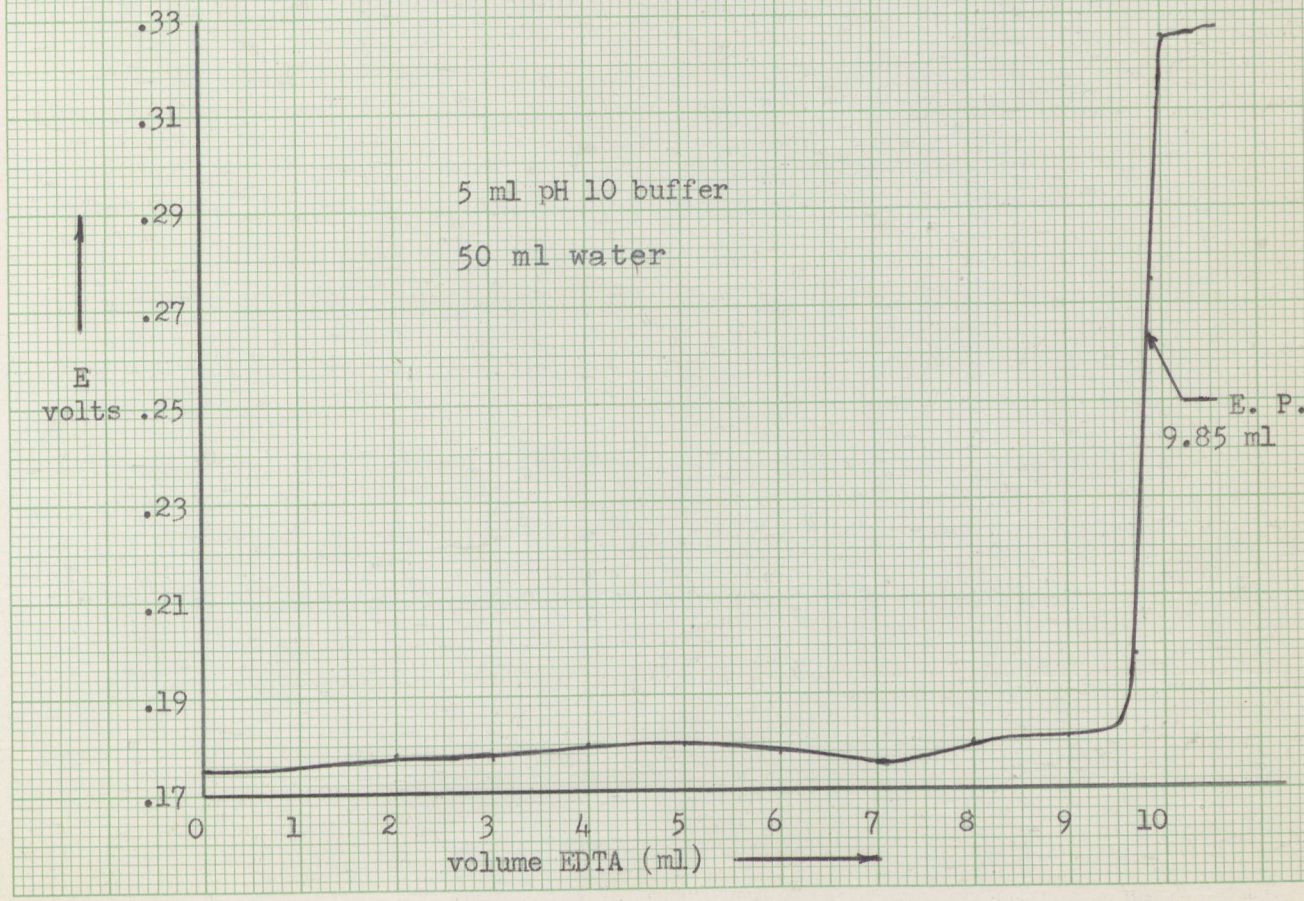


TABLE 3

Titration of Zinc

(Bismuth amalgam electrode washed with hot 9M H_2SO_4)

10 ml 0.0997M Zn^{++}, 1 drop sat BiEDTA, 1 drop sat HgEDTA, titrate with 0.1021M EDTA

5 ml pH 10 buffer
75 ml water

volume	E_{cell}
0.00 ml	0.175 volts
2.00	0.174
4.00	0.174
6.00	0.177
8.00	0.180
9.00	0.183
9.50	0.190
9.70	0.218
9.90	0.318
10.10	0.350

mmoles Zn taken: 0.997
found: 1.001
error: +0.4%

2 ml pH 10 buffer
75 ml water

volume	E_{cell}
0.00 ml	0.103 volts
2.00	0.103
4.00	0.104
6.00	0.104
8.00	0.104
8.50	0.105
9.00	0.105
9.20	0.106
9.40	0.108
9.60	0.110
9.80	0.254
10.00	0.270
10.20	0.270

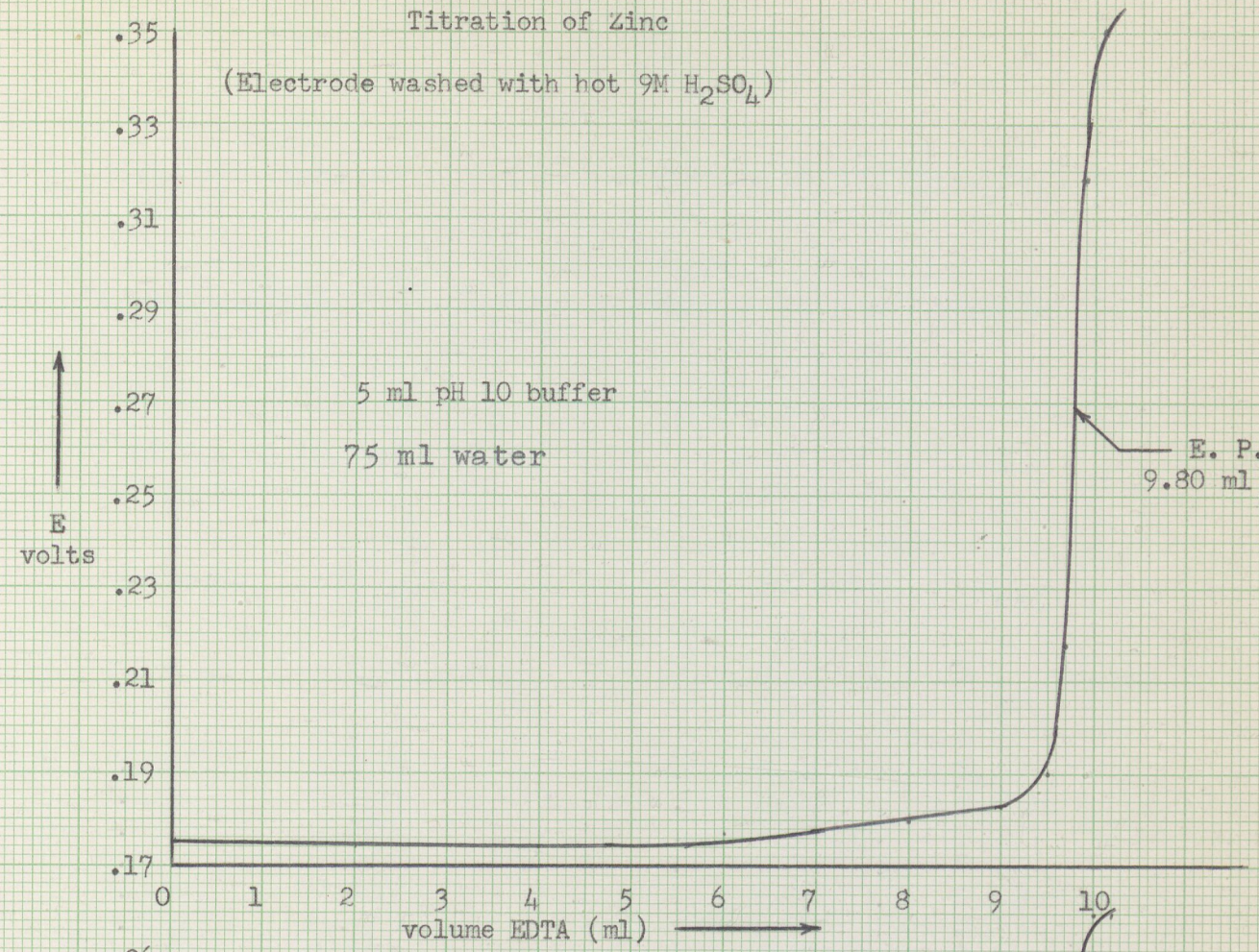
mmoles Zn taken: 0.997
found: 0.997
error: zero

Remarks: In both experiments, the electrode required 15 minutes to come to initial equilibrium and 5 minutes to stabilize with each addition near the end point.

FIGURE 7

Titration of Zinc

(Electrode washed with hot 9M H_2SO_4)



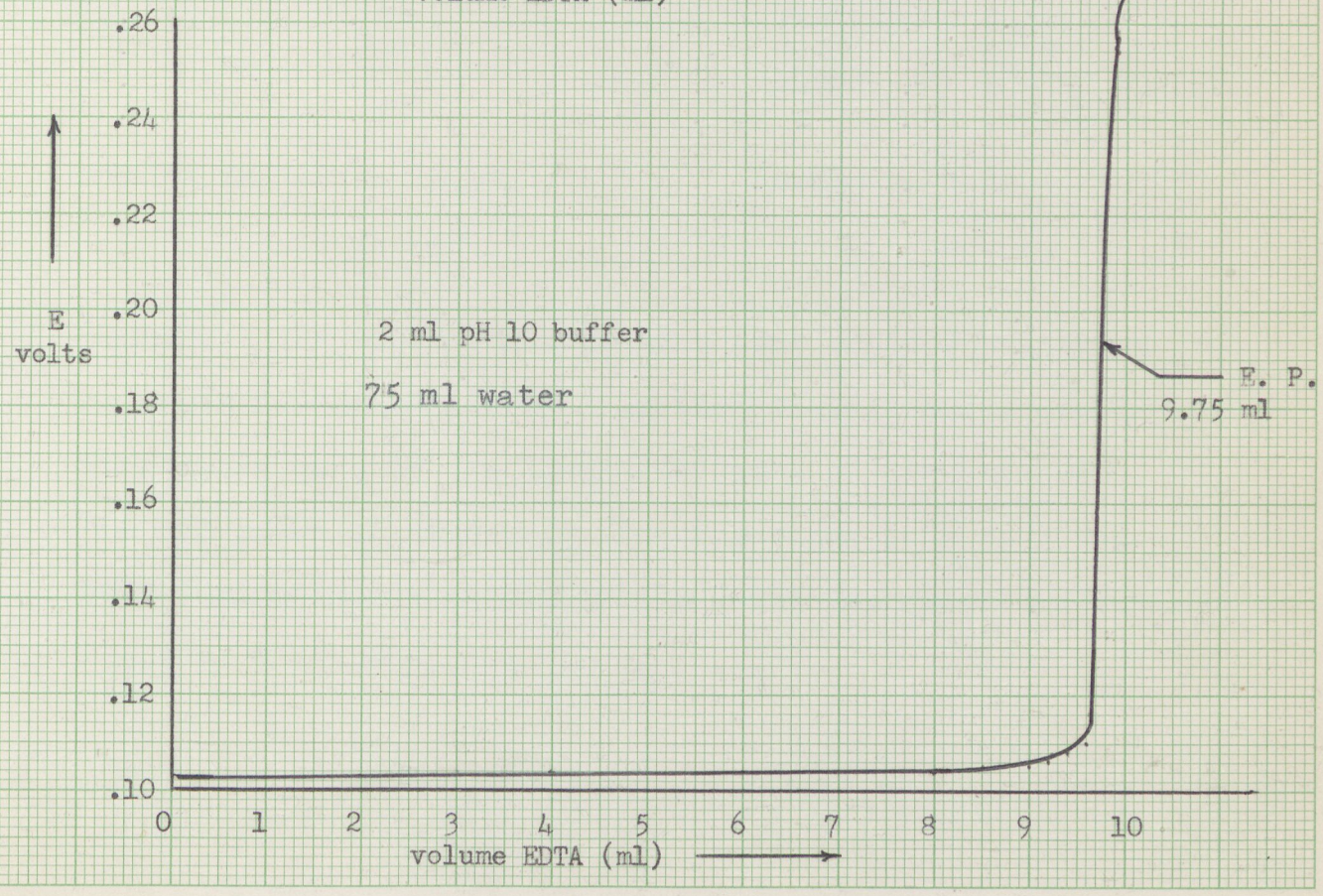


TABLE 4

(Bismuth amalgam electrode washed with hot 9M H_2SO_4)

10 ml 0.0997M Zn^{++}, 1 drop BiEDTA, 1 drop sat HgEDTA, titrate with 0.1021M EDTA

5 ml pH 10 buffer
150 ml water

volume	E_{cell}
0.00 ml	0.078 volts
2.00	0.078
4.00	0.078
6.00	0.079
8.00	0.080
9.00	0.080
9.40	0.081
9.60	0.083
9.70	0.175
9.80	0.280
9.90	0.281

mmoles Zn taken: 0.997
found: 0.994
error: -0.3%

2 ml pH 10 buffer
150 ml water

volume	E_{cell}
0.00 ml	0.075 volts
2.00	0.075
4.00	0.075
6.00	0.075
8.00	0.076
9.00	0.077
9.50	0.078
9.60	0.080
9.70	0.158
9.80	0.261
9.90	0.277
10.00	0.278

mmoles Zn taken: 0.997
found: 0.996
error: -0.1%

Remarks: The electrode came to a more rapid equilibrium in these dilute solutions. Initial stabilization took 10 minutes and, of the three additions of titrant near the end point in each case, the first and last required only 2 minutes for stabilization while the middle addition required 5 minutes.

FIGURE 8

Titration of Zinc

(Electrode washed with 9M H_2SO_4)

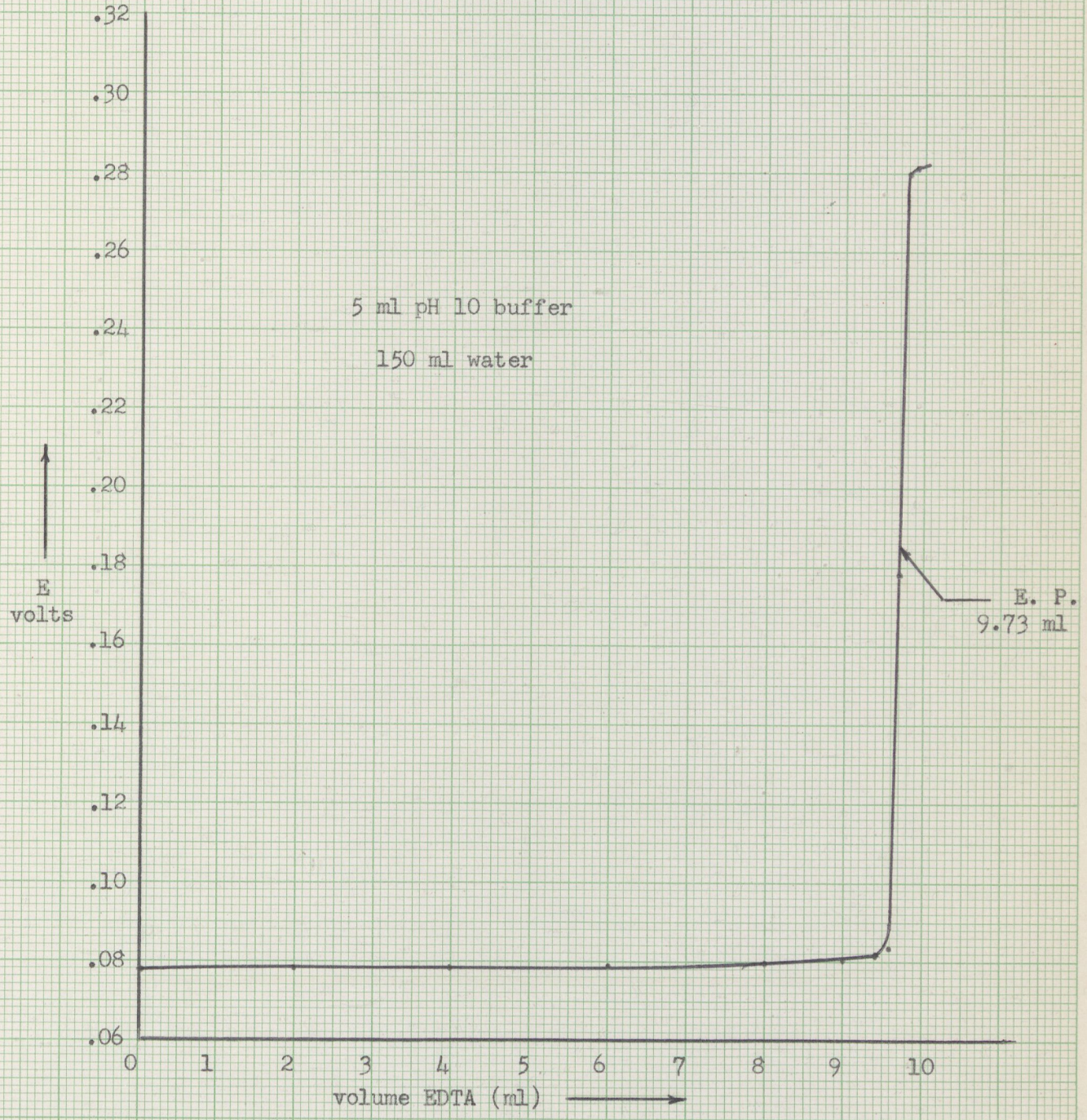


FIGURE 9

Titration of Zinc

(Electrode washed with 9M H_2SO_4)

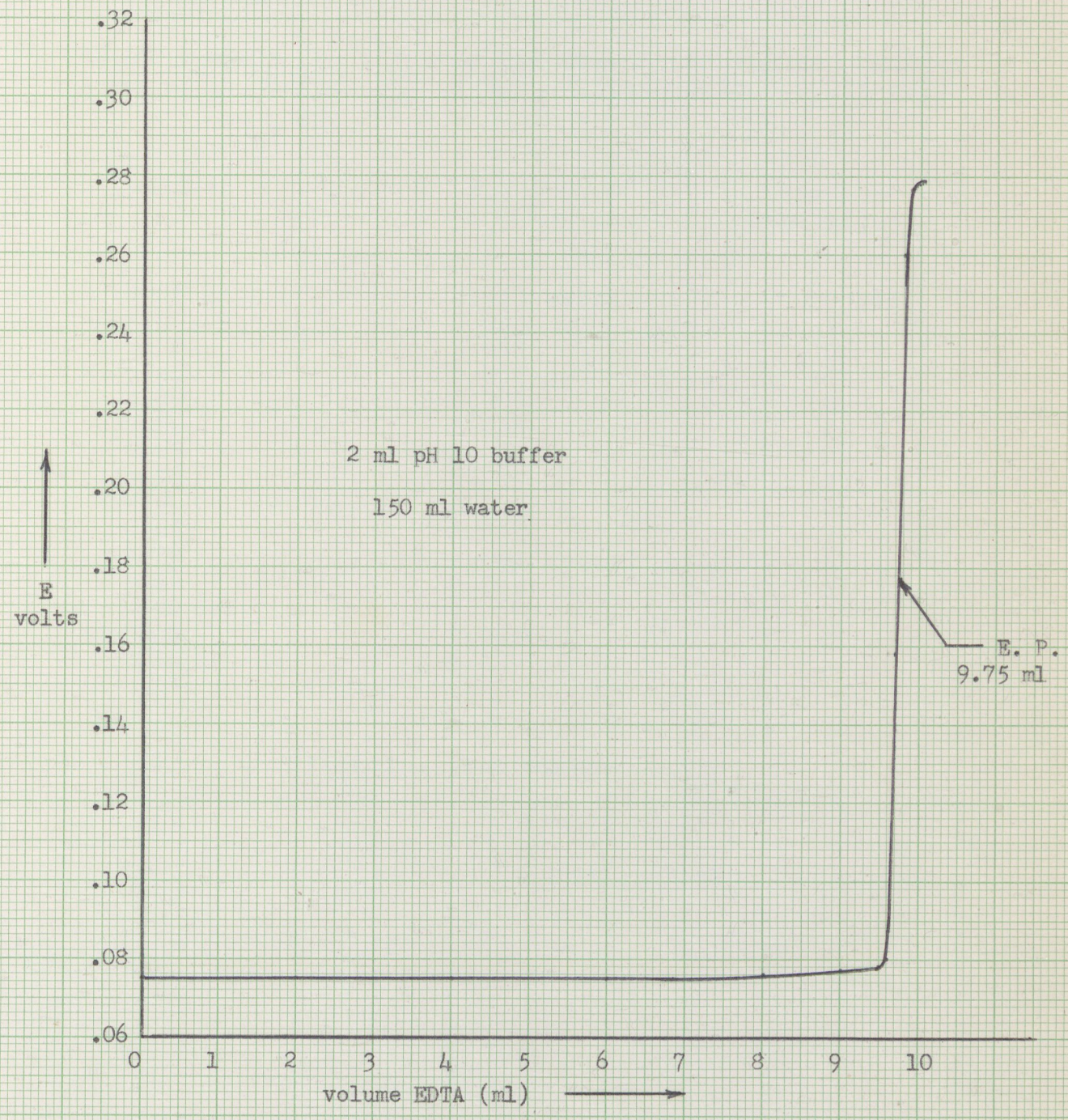


TABLE 5

Titration of Zinc

(Bismuth amalgam electrode washed with hot H_3PO_4)

10 ml 0.0997M Zn^{++}, 1 drop sat BiEDTA, 1 drop sat HgEDTA, 2 ml pH 10 buffer, 150 ml H_2O, titrate with 0.1021M EDTA

volume	E_{cell}	time to stabilize
0.00 ml	0.083 volts	10 min
2.00	0.085	1
4.00	0.084	0
6.00	0.082	0
8.00	0.086	0
9.00	0.086	0
9.20	0.087	0
9.40	0.089	0
9.50	0.090	0
9.65	0.095	3
9.70	0.143	5
9.80	0.265	5
9.90	0.279	3
10.00	0.280	0
10.20	0.277	0

millimoles zinc taken: 0.997

found: 0.994

error: -0.3%

FIGURE 10

Titration of Zinc

(Electrode washed with hot con. H_3PO_4)

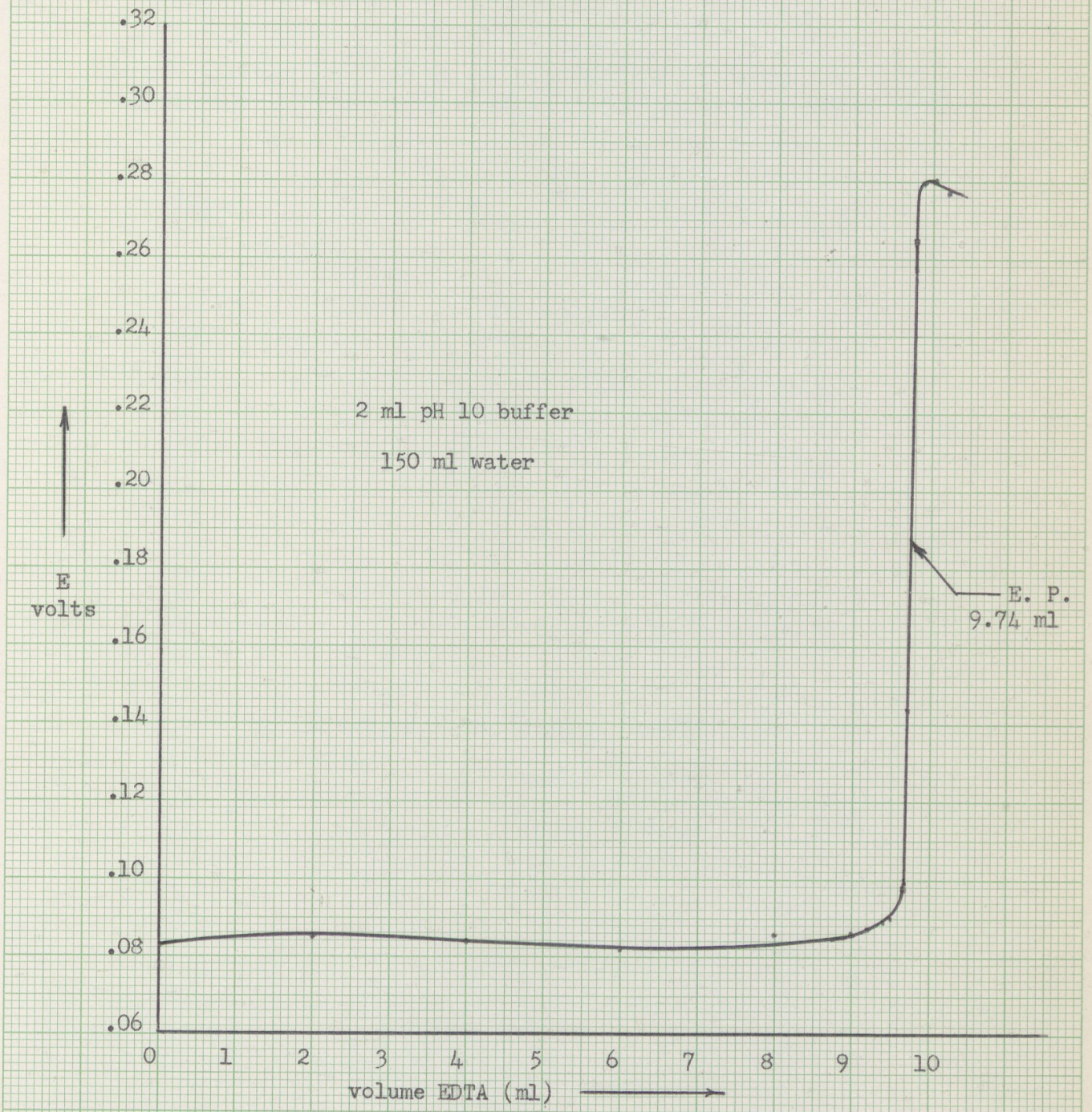


TABLE 6

Titration of Zinc

(Electrode washed with hot 9M H_2SO_4 and polished)

10 ml 0.0997M Zn^{++}, 1 drop sat BiEDTA, 1 drop sat HgEDTA, 2 ml pH 10 buffer, 150 ml H_2O, titrate with 0.1021M EDTA

volume	E_{cell}	time to stabilize
0.00 ml	0.066 volts	5 min
2.00	0.066	0
4.00	0.066	0
6.00	0.067	0
8.00	0.067	0
9.00	0.068	0
9.50	0.071	0
9.60	0.071	1
9.70	0.127	1
9.80	0.238	1
9.90	0.282	1
9.95	0.284	0
10.20	0.283	0

millimoles zinc taken: 0.997

found: 0.996

error: -0.1%

FIGURE 11

Titration of Zinc

(Electrode washed with hot 9M H_2SO_4 and polished)

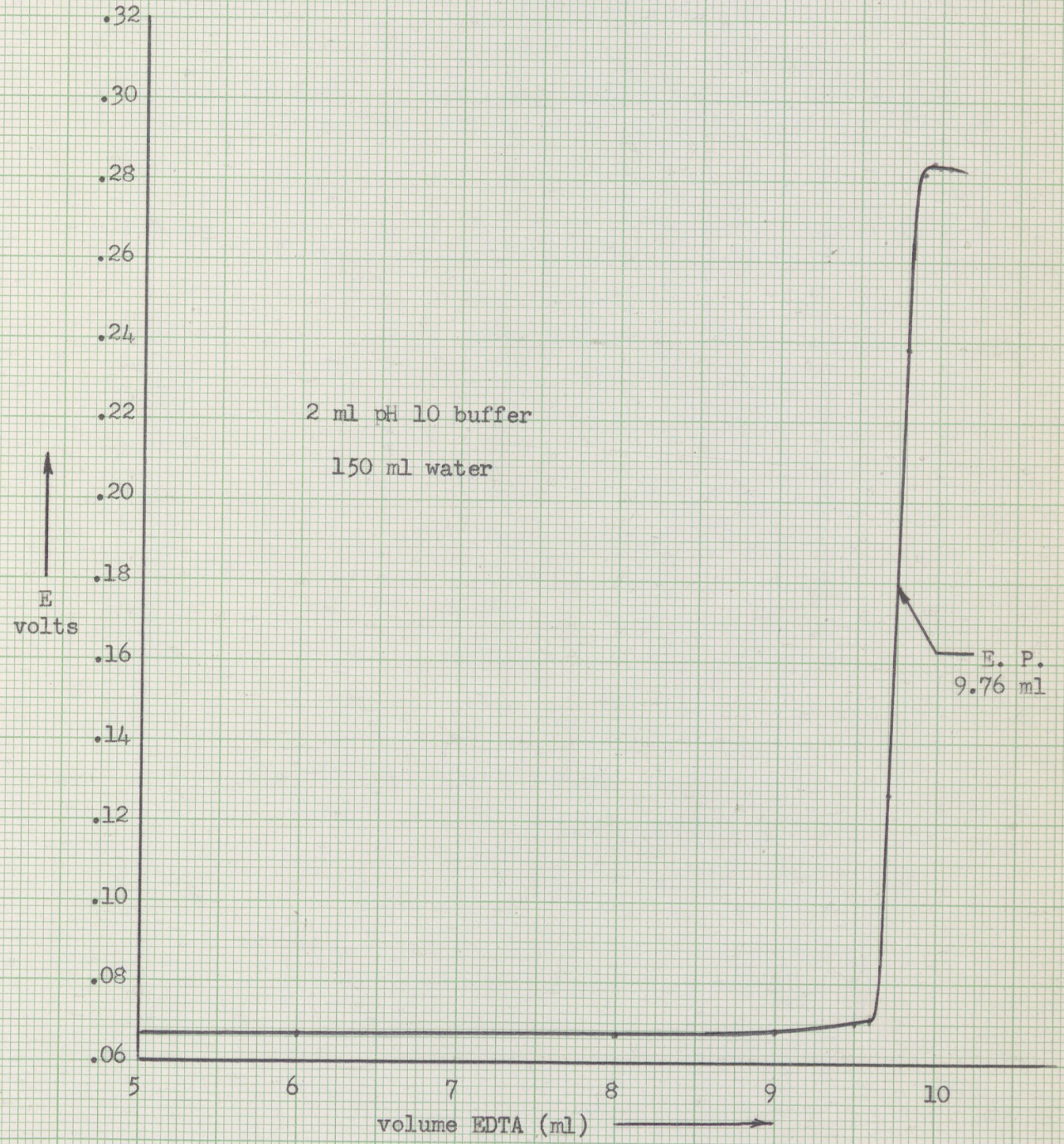


TABLE 7

Titration of Copper

(Electrode washed in hot 9M H_2SO_4 and polished)

10 ml 0.1032M Cu^{++}, 1 drop sat BiEDTA, 1 drop sat HgEDTA, 20 drops pH 10 buffer, 150 ml H_2O, 0.1021M EDTA as titrant

volume	E_{cell}	time to stabilize
0.00 ml	0.054 volts	10 min
2.00	0.054	0
4.00	0.056	0
6.00	0.059	1
8.00	0.066	1
9.00	0.072	2
9.50	0.082	2
9.70	0.099	2
9.90	0.124	2
10.00	0.203	3
10.10	0.304	3
10.20	0.301	2
10.40	0.302	0

millimoles copper taken: 1.032

found: 1.025

error: -0.6%

FIGURE 12

Titration of Copper

(Electrode washed in hot 9M H_2SO_4 and polished)

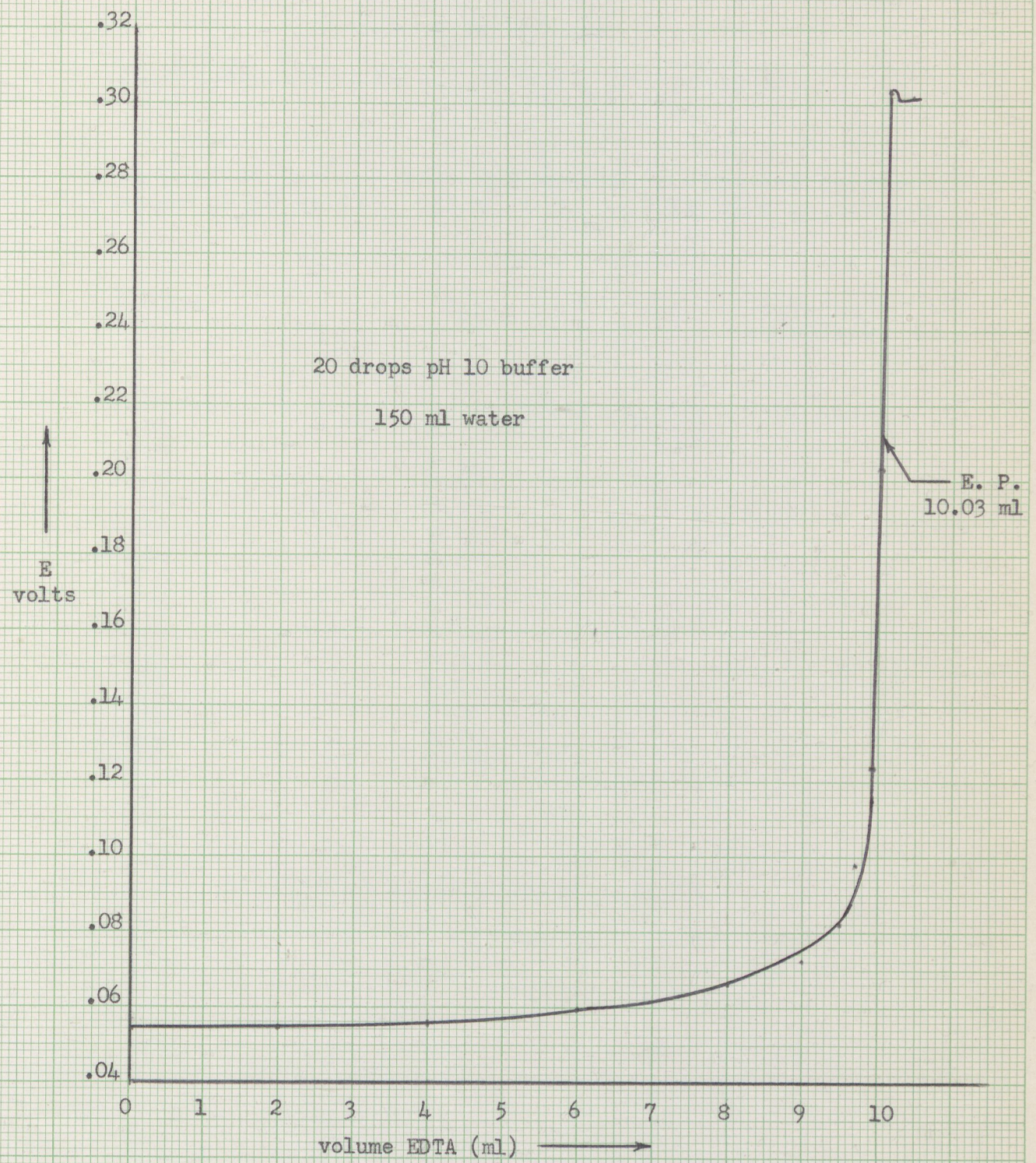


TABLE 8

Titration of Calcium

(Electrode washed in hot 9M H_2SO_4 and polished)

10 ml 0.1014M Ca^{++}, 1 drop sat BiEDTA, 1 drop sat HgEDTA, 25 drops pH 10 buffer, 150 ml H_2O, 0.1021M EDTA as titrant

volume	E_{cell}	time to stabilize
0.00 ml	0.128 volts	10 min
2.00	0.129	0
4.00	0.128	0
6.00	0.131	0
8.00	0.134	0
9.00	0.137	1
9.40	0.141	1
9.60	0.147	2
9.70	0.150	1
9.80	0.156	3
9.95	0.202	4
10.05	0.291	6
10.10	0.297	1
10.20	0.297	0
10.40	0.296	0

millimoles calcium taken: 1.014

found: 1.016

error: 0.2%

FIGURE 13

Titration of Calcium

(Electrode washed in hot 9M H_2SO_4 and polished)

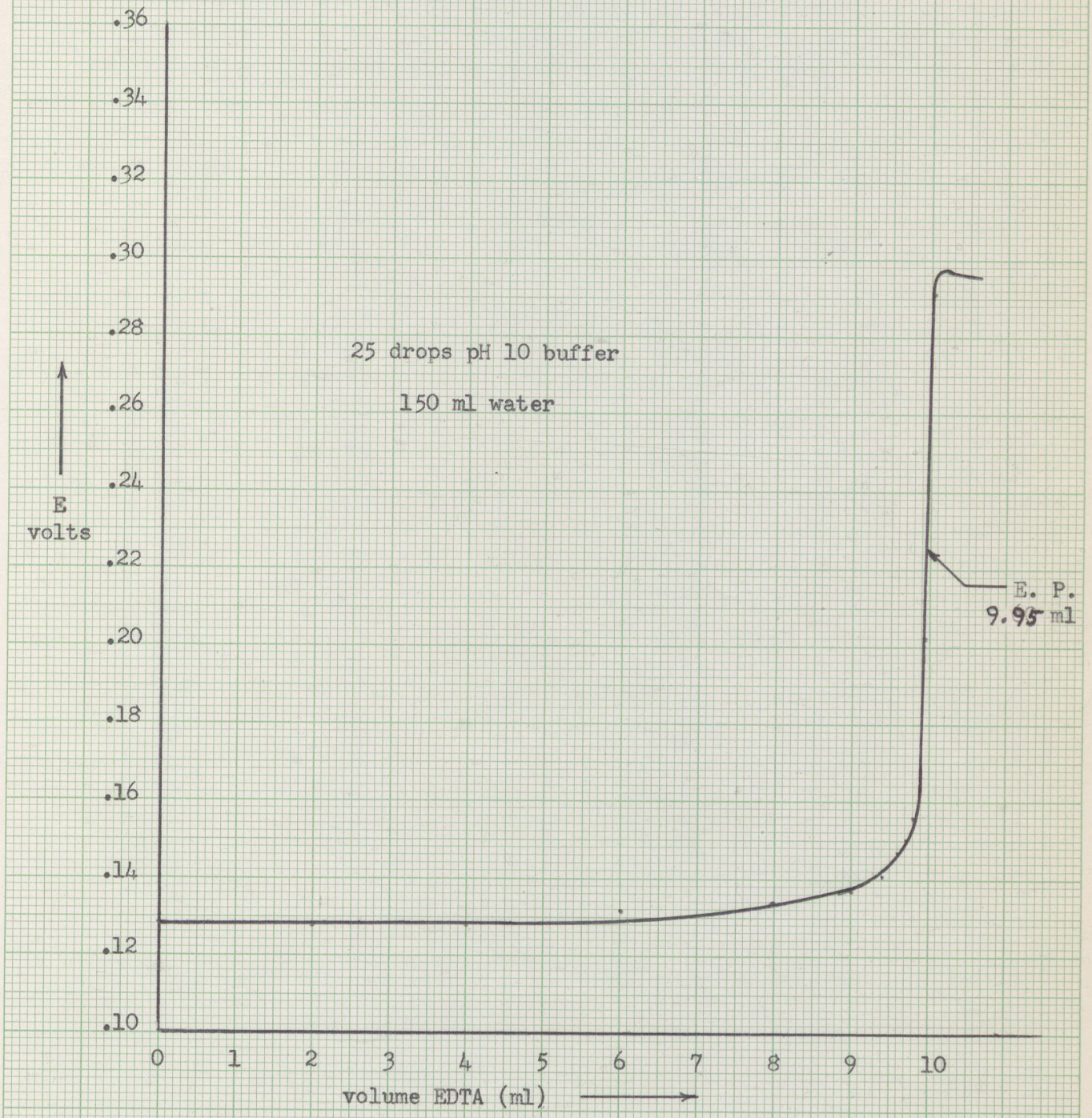


TABLE 9

Titration of Mixtures

10 ml 0.0997M Zn^{++} PLUS 10 ml of either 0.1014M Ca^{++} or 0.1032M Cu^{++}, 2 ml pH 10 buffer, 150 ml water, wash electrode with H_2SO_4 and polish, titrate with 0.1021M EDTA

Zinc and Calcium

volume	E_{cell}
0.00 ml	0.092 volts
2.00	0.093
4.00	0.093
6.00	0.094
8.00	0.096
9.00	0.098
9.40	0.098
9.80	0.098
10.00	0.099
10.20	0.100
11.00	0.101
12.00	0.102
14.00	0.104
16.00	0.103
18.00	0.106
19.00	0.110
19.40	0.116
19.60	0.160
19.80	0.210
20.00	0.260
20.20	0.266
20.30	0.266

millimoles taken: 2.011

found: 2.005

error: -0.3%

Zinc and Copper

volume	E_{cell}
0.00 ml	0.070 volts
2.00	0.070
4.00	0.070
6.00	0.071
8.00	0.071
9.00	0.072
9.60	0.072
10.00	0.072
11.00	0.073
12.00	0.073
14.00	0.074
16.00	0.076
18.00	0.082
19.00	0.086
19.40	0.091
19.60	0.094
19.80	0.100
20.00	0.115
20.20	0.202
20.40	0.278
20.60	0.294
21.00	0.293

millimoles taken: 2.029

found: 2.033

error: 0.2%

FIGURE 14

Titration of Mixtures

(Electrode washed in hot H_2SO_4 and polished)

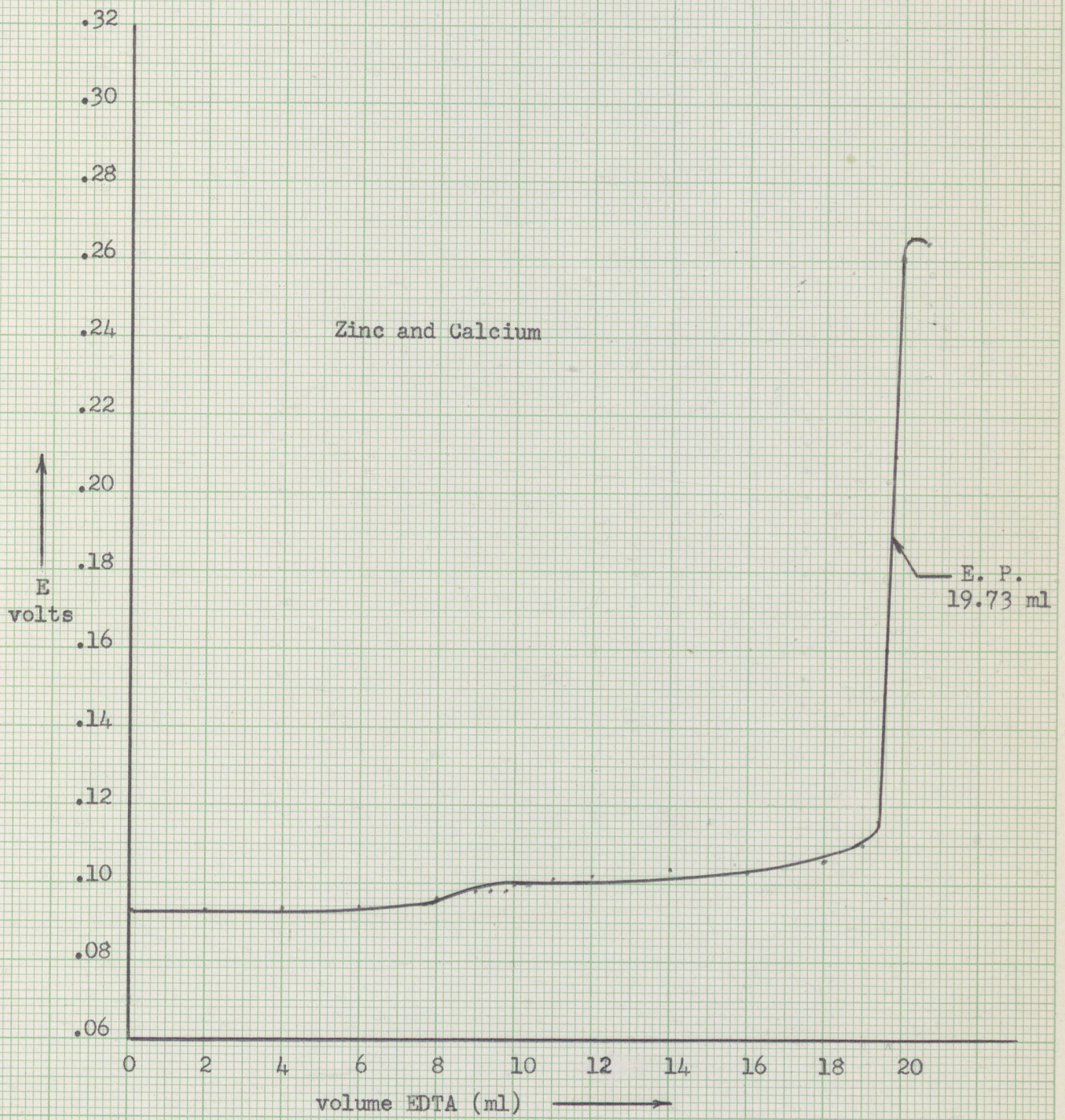


FIGURE 14 (cont'd)

Titration of Mixtures

(Electrode washed in hot 9M H_2SO_4 and polished)

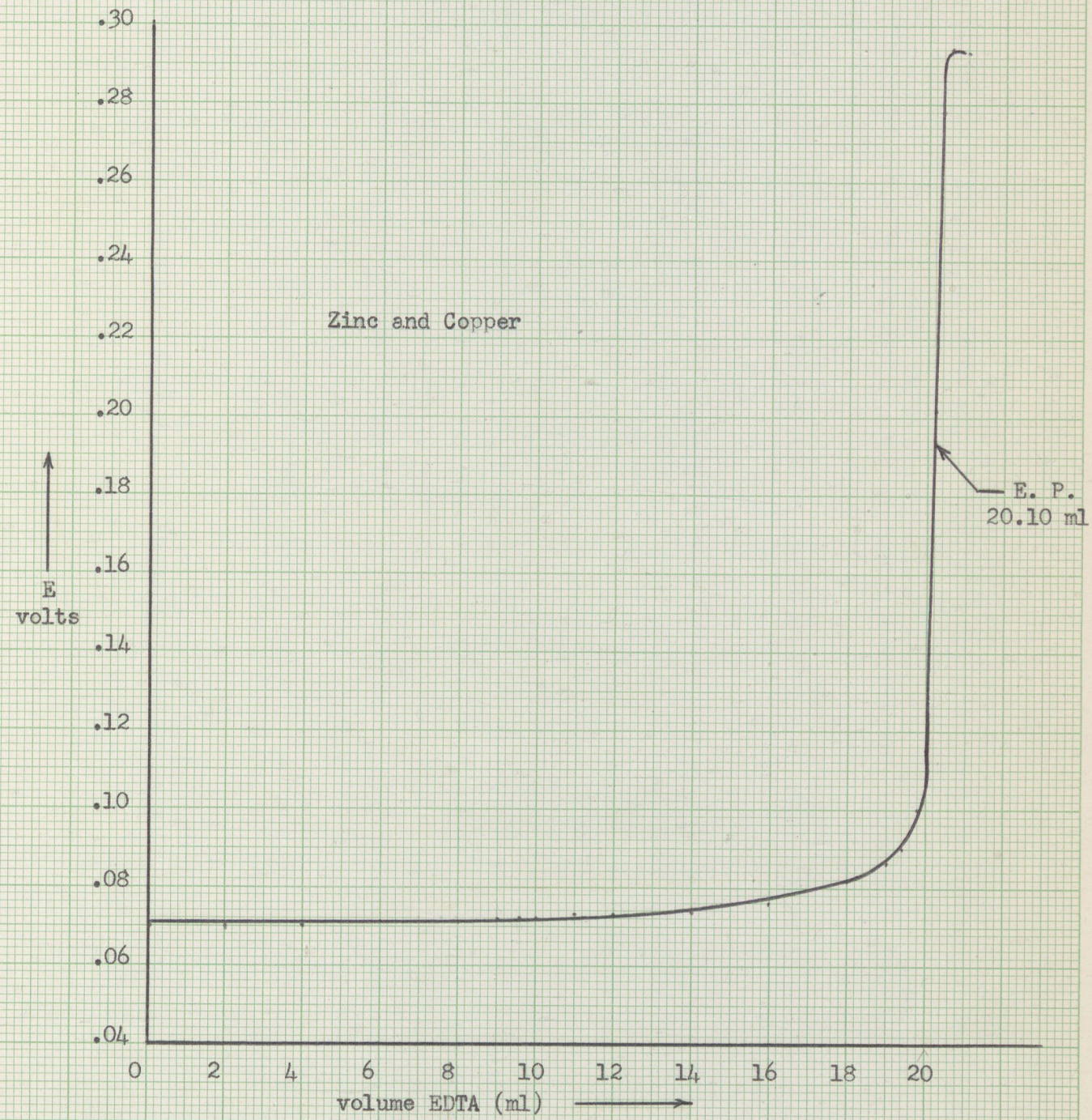


TABLE 10

Titration of Zinc Using the Automatic Titrator

10 ml 0.0997M Zn^{++}, 1 drop sat BiEDTA, 1 drop sat HgEDTA, 150 ml H_2O, titrate with 0.1021M EDTA, wash electrode with hot 9M H_2SO_4; automatic titrator set at polarity 2 and 2nd derivative voltage

sample number	volume pH 10 buffer	ml EDTA	time for titration	ml EDTA per sec	millimoles Zn found	% error from taken	deviation from ave. millimoles
1	1 ml	10.54	90 sec	0.117	1.078	8.1	α
2[β]	2 ml	15.00	210	0.071	β	β	β
3	2 ml	10.35	125	0.083	1.056	5.9	+0.033
4	1 ml	10.16	130	0.079	1.037	4.0	+0.014
5	40 drops	9.80	125	0.078	1.001	0.3	-0.022
6	20 drops	9.95	120	0.083	1.016	2.0	-0.007
7	40 drops	10.02	135	0.075	1.024	2.7	+0.001
8	1 ml	9.83	115	0.085	1.004	0.7	-0.019

α Sample number 1 was not taken into consideration in calculating the standard deviation since the delivery rate of EDTA was much too fast.

β The delivery rate of EDTA in sample number 2 was too slow to provide an end point change in potential large enough or fast enough for the titrator thyratron to fire.

The mean amount of zinc found is 1.023 millimoles. The standard deviation of the mean is 0.018. The probable error of the mean is 0.675 x 0.018 = 0.012

SUMMARY

The experimental results determined in this research show excellent agreement with the considerations propounded in the theory section. Because of the very high stability constant of the bismuth-EDTA complex, the potential break at the end points of titrations are greater when using the bismuth amalgam electrode than when using the mercury electrode alone. By adjusting the titration conditions, the end point breaks have been measured over 200 mv when titrating zinc or copper and over 170 mv when titrating calcium.

These results have been achieved primarily by controlling the poisoning effects of bismuth oxide on the electrode. Smoothing and rounding the contours of the bismuth prevents impurities from lodging in crevices. Vigorous washing with sulfuric or phosphoric acid effectively eliminates the oxides which do form as does polishing with paper towels. Deaeration of solutions should also have the effect of reducing the small electrode drift (less than 0.1 mv per minute) in basic media.

In accordance with the apparent stability constant equation (19) is the fact that the largest end point breaks occur when the minimum amount of combined buffer-auxiliary complexing agent (NH_3-NH_4^+) is present. This optimum

volume of pH 10 buffer has been found to be from 20 drops to 2 ml.

The increase in end point breaks with decreasing metal ion concentration follows from the Nernst equation (8). In this work the best results have been realized when the metal ion was present in a concentration of less than 0.001M. In the case of zinc there was about 40 mg of metal per 100 ml of solution.

Also as was predicted in the theory section, the addition of a small amount of BiEDTA and HgEDTA to the titration mixture improves the kinetics of the electrode reaction enabling the electrode to attain good poise, rapid equilibrium, and excellent stability. These two complexes are equally valuable to a titration although whichever complex is added first is seen to have the greater effect. Despite the fact that the electrode requires 2-6 minutes to achieve final equilibrium at the end point, it is capable of passing through a 100 mv change in 75 seconds.

The preferential titration of individual components of a mixture, while not accomplished in this work, is still a distinct possibility if an acid buffer is used which contains neither chloride nor acetate ions. In addition to a judicious use of the pH effect to analyze mixtures, auxiliary complexing agents such as CN^- can be employed to mask some metals of a mixture while the others are titrated.

On the automatic titrator, since much of the variation in readings was due to uneven rate of delivery of EDTA, the use of a constant delivery rate burette would undoubtedly yield more precise results. Hopefully, the standard deviation, which has been calculated to be almost 2% of the mean, can be decreased. Slight differences from solution to solution may also have an exaggerated effect on the rate of change of potential at the end point.

Even greater accuracy than the average of 0.3% obtained in manual titrations can be expected if the standard EDTA solution is more dilute than the 0.1M solutions used in this work. The use of a 0.01M EDTA solution as titrant would reduce the error inherent in reading the burette. Where the end point now occurs within a range of 0.2 ml, it would then occur in the space of 2 ml.

CONCLUSION

The bismuth amalgam electrode has been shown to yield reproducible and accurate results with end point breaks considerably larger than those obtained with other electrode systems. The solution conditions necessary for the best results, such as buffer and metal ion concentration, electrode preparation techniques, and the stabilizing effect of BiEDTA and HgEDTA, have been determined. Limitations on the electrode (relatively slow end point equilibrium and reactivity with halides, oxygen, and acetate) have been studied and should not detract significantly from the wide applicability and broad potential of this electrode.

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